

MOSSBAUER AND SPECTRAL (VISIBLE AND NEAR-IR) DATA FOR Fe^{3+} -SUBSTITUTED RUTILE; H. V. Lauer Jr. (LESC, Houston, Tx 77058), R. V. Morris (NASA/JSC, Houston, Tx 77058), and R. K. Vempati (Lamar University, Beaumont, Tx)

INTRODUCTION: Titanohematite and rutile containing some Fe^{3+} are possible highly oxidized weathering products of ilmenite and titanomagnetites. We report here Mossbauer and reflectivity data (visible and near-IR) for Fe^{3+} -substituted rutile as a part of our continuing studies of ferric-substituted minerals that might have bearing on the interpretation of Martian spectral data.

SAMPLE PREPARATION: Appropriate amounts of titanous chloride and ferric chloride were mixed together in a polyethylene beaker. To 25 - 30 ml of this solution, 100 ml of 7M sodium hydroxide was added while constantly stirring. After the entire NaOH solution was added, the entire contents of the beaker (brown precipitate + supernate) was aerated by pouring it back and forth between two beakers several times. The solution was then allowed to incubate for an hour. After washing the precipitate several times in deionized water, the supernate was poured off and the precipitate was dialyzed against deionized water for three weeks. Several times a day the dialysis water was changed and the dialysis bag was washed off and rotated to stir its contents. With time the precipitate slowly changed color to a light yellow tan. Once the contents of the dialysis bag appeared to be uniform in color and no more color changed was observed, the contents of the bag was washed and transferred back to a 1 L polyethylene beaker. The volume of the solution was increased to 500 ml using 0.3M NaOH. The beaker was covered with a watch glass and incubated at 70 C in a convection oven for 48 hrs. After cooling the resulting precipitate was again dialyzed against deionized water for a week. The dialyzed material was freeze dried and then calcined in air for 40 hrs at 500, 650, 800, 1000 C. The only polymorph of TiO_2 stable above 700 C is rutile.

RESULTS AND DISCUSSION: We will discuss result for five of the samples heated to 1000 C. They will be referred to as RuF(i)/1000 with $i = 1 - 5$ referring to the starting sample ID. The iron content in the sample increases with i ($i = 0$ is undoped). Fig. 1 shows the reflectivity spectra for RuF0/1000 through RuF5/1000. Their room-temperature Mossbauer spectra were all ferric doublets in octahedrally coordinated sites ($\text{IS} \sim 0.36 \text{ mm/s}$).

Comparing the reflectivity spectrum of RuF0/1000 to those of RuF(1 - 5)/1000 shows that the increased depth of the spectral features is consistent with increasing Fe^{3+} content in each successive sample. Also, the reflectivity spectra of RuF(1,2,3) are similar, and RuF(4,5) are similar. This same grouping is also found in the quadrupole splittings, with the first group having distinctly lower quadrupole splittings (0.36 versus 0.60 mm/s). The reason for the difference is not clear, but the local environment of ferric iron clearly changes between the RuF3/1000 and RuF4/1000 samples. It may be that the pair transition shifts to lower energies and thus obscures the band minima at $\sim 875 \text{ nm}$ (${}^6\text{A}_1 \rightarrow {}^4\text{T}_{2g}$) and 475 nm (${}^6\text{A}_1 \rightarrow {}^4\text{E}, {}^4\text{A}$).

FIGURE 1



